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CIRCULATING FILTRATION METHOD FOR LIQUID FILTERING DEVICE

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[There are no amendments to this patent.]

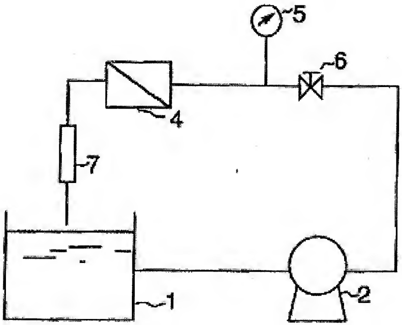
Abstract

Objective

The objective of the present invention is to provide an operation method, which can prevent decrease of flux permeated through a membrane due to the air lock phenomenon to maintain high permeability in a full-filtration type liquid filtering device using a hydrophilized membrane made of a fluorine-type high-molecular-weight polymer.

Constitution

In a full-filtration type liquid filtering device connected to a liquid supply tank and having a hydrophilized membrane made of a fluorine type high-molecular-weight polymer installed in a container, the liquid to be treated is circulated and filtered under a pressure higher than the bubble point of the hydrophilized membrane. Also, in a full-filtration type liquid filtering device connected to a liquid supply tank, having a bypass valve connected in the filtering device or in front of the filtering device, and having a hydrophilized membrane made of a fluorine type high-molecular-weight polymer installed in a container, the bypass valve is opened intermittently during pressurized filtration of the liquid to be treated to significantly lower the pressure in said container.



Claims

1. A circulating filtration method for a liquid filtering device, characterized by the fact that in a full-filtration type liquid filtering device connected to a liquid supply tank and having a hydrophilized membrane made of a fluorine type high-molecular-weight polymer installed in a container, the liquid to be treated is circulated and filtered under a pressure higher than the bubble point of the hydrophilized membrane.

2. A circulating filtration method for a liquid filtering device, characterized by the fact that in a full-filtration type liquid filtering device connected to a liquid supply tank, having a

bypass valve connected in the filtering device or in front of the filtering device, and having a hydrophilized membrane made of a fluorine type high-molecular-weight polymer installed in a container, the bypass valve is opened intermittently during pressurized filtration of the liquid to be treated to significantly lower the pressure in said container.

3. The circulating filtration method for a liquid filtering device described in Claim 1 or 2, characterized by the fact that the liquid to be treated is ammonia water or other liquid containing a foaming substance or liquid containing bubbles.

4. The circulating filtration method for a liquid filtering device described in Claim 1 or 2, characterized by the fact that the fluorine type high-molecular-weight polymer is polytetrafluoroethylene, polyfluorovinylidene, tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention pertains to a circulating filtration method for a liquid filtering device used for precise filtration or ultrafiltration of liquids, such as chemical liquid, food in liquid form, washing water, etc.

[0002]

Prior art

During precise filtration or ultrafiltration of a chemical liquid, food in liquid form, washing water, or other hydrophilic liquids, the particle removability, the liquid flux permeated through a membrane, the chemical resistance, the pressure durability, heat resistance, etc., are important factors of the filtering membrane. Therefore, a porous membrane made of polytetrafluoroethylene (PTFE), polyfluorovinylidene or other fluororesins, polyethylene, polypropylene, polysulfone, or other high-molecular-weight polymers has been used as filtering membrane.

[0003]

Since said porous membranes are hydrophobic, these membranes are used after they are hydrophilized by organic solvents, etc., having low surface tension as a pretreatment in a treatment using hydrophilic liquid. In the semiconductor industry, however, silicon wafers are washed with nitric acid, hydrofluoric acid, sulfuric acid, etc. When the chemical is discharged during replacement of the chemical after circulated washing, if air flows into the cartridge filter for filtration, the effect of hydrophilizing the hydrophobic film will disappear. In other words, if

the air has contact with the surface of the hydrophilized hydrophobic membrane, such as PTFE membrane, in the filter, the organic solvent or other hydrophilizing agent will dry up, and the hydrophilizing effect will disappear. As a result, when the chemical is fed in the next round, the flux permeated through a membrane will decrease significantly. Therefore, it is necessary to hydrophilize the membrane using an organic solvent or other hydrophilizing agent again.

[0004]

In order to solve this problem, the fluororesin porous membrane itself is hydrophilized. For example, Japanese Kokai Patent Application No. Sho 61[1986]-249502 discloses a method that coats a surfactant. As described in Japanese Kokai Patent Application No. Sho 56[1981]-63772 or Hei 1[1989]-98640, a water-soluble polymer, such as acrylic acid or polyvinyl alcohol, is impregnated in the pores of a porous membrane. The polymer is converted into an insoluble polymer after undergoing heat treatment, treatment with acetal, esterification treatment, treatment with dichromatic acid, treatment with ionizing radiation, etc. Also, as described in Japanese Kokai Patent Application No. Hei 2[1990]-196834, an ArF laser is radiated on the fluororesin to modify its surface for hydrophilization.

[0005]

When the membrane hydrophilized this way is used to carry out filtration, there is no need to perform pretreatment in order to filter hydrophilic liquid. However, if the bubbles generated in the liquid are present on the membrane surface, because of hydrophilization, the bubble point (pressure under which bubbles start to permeate through the wet membrane) rises compared with that of the hydrophobic membrane. Since the bubbles cannot permeate through the membrane under a pressure lower than said high bubble point, air lock phenomenon occurs, and the flux permeated through the membrane is reduced. In particular, when a liquid containing a foaming substance, such as hydrogen peroxide water, is used, the decrease of the flux permeated through the membrane is significant, and it is necessary to perform the air removing operation frequently.

[0006]

On the other hand, for cross-flow type precise filtration of liquid containing solid particles, in order to obtain high flux permeation against clogging of the filtering membrane, a method that stops a pump intermittently is disclosed in Japanese Kokai Patent Application No. Sho 63[1988]-125611. For the cross-flow type, the liquid to be treated flows in parallel with the filtering membrane so that the air lock phenomenon will not occur. There is no description in this

publication regarding a full-filtration type filtering device using a hydrophilized membrane made of a fluorine-type high-molecular-weight polymer.

[0007]

Problems to be solved by the invention

For a hydrophilized membrane made of a fluorine high-molecular-weight polymer, the bubbles generated in the liquid are present on the membrane surface; because of hydrophilization, the bubble point rises compared with that of the hydrophobic membrane. Since the bubbles cannot permeate through the membrane under a pressure lower than said high bubble point, air lock phenomenon occurs, and the flux permeated through the membrane is reduced. The objective of the present invention is to provide an operation method, which can prevent a decrease in the flux permeated through a membrane due to the air lock phenomenon to maintain high permeability in a full-filtration type liquid filtering device using a hydrophilized membrane made of a fluorine-type high-molecular-weight polymer.

[0008]

Means to solve the problems

The present invention provides a method that circulates and filters a liquid to be treated under a pressure higher than the bubble point of a hydrophilized membrane in a full-filtration type liquid filtering device connected to a liquid supply tank and having said hydrophilized membrane made of a fluorine type high-molecular-weight polymer installed in a container. The present invention also provides a method characterized by the fact that in a full-filtration type liquid filtering device connected to a liquid supply tank, having a bypass valve connected in the filtering device or in front of the filtering device, and having a hydrophilized membrane made of a fluorine type high-molecular-weight polymer installed in a container, the bypass valve is opened intermittently during pressurized filtration of the liquid to be treated to significantly lower the pressure in said container.

[0009]

The hydrophilized membrane made of fluorine type high-molecular-weight polymer used in the present invention is obtained by hydrophilizing fluorine-type high-molecular-weight polymer membrane made of polytetrafluoroethylene (PTFE), polyfluorovinylidene (PVDF), tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), tetrafluoroethylene-ethylene copolymer (ETFE), polychlorotrifluoroethylene (CTFE), etc. In particular, PTFE is preferred in consideration of chemical resistance and heat resistance. Either a sintered product or non-sintered product can be

used. The pore size of the membrane is preferred to be 0.01-10 μm, preferably in the range of 0.03-0.2 μm.

[0010]

There is no special limitation on the hydrophilizing method of said membrane. For example, it is possible to use a method that coats a surfactant, a method that impregnates acrylic acid, polyvinyl alcohol, polyethylene glycol, or other water-soluble polymer in the pores of the membrane and hydrophilizes the polymer by performing heat treatment, acetalization treatment, esterification treatment, dichromatic acid treatment, or irradiation with ionizing radiation, or a method that impregnates aluminum hydroxide, boric acid, lithium hydroxide, or other compounds having hydrophilic groups in the pores of the membrane, followed by irradiating with UV light, or the method that performs hydrophilization by irradiating an ArF laser.

[0011]

Since the hydrophilized membrane of the fluorine type high-molecular-weight polymer has good chemical resistance and heat resistance, the filtration method disclosed in the present invention can be suitably used to treat acid, alkali, organic solvent (liquid containing mixed bubbles), as well as hydrogen peroxide water, ammonia water, or other liquids containing a foaming substance (liquid that generates bubbles). The bubble point mentioned in the present invention refers to the pressure under which bubbles are first generated from the membrane material when air is supplied after the membrane is filled with liquid. It varies depending on the liquid type, membrane material, membrane pore size, and membrane thickness. For example, in the case of PTFE membrane, the bubble point in an aqueous system is usually in the range of 0.4-6 kg/cm^2. For a hydrophilized PTFE membrane, the bubble point in the aqueous system is usually as high as 3-10 kg/cm^2. When a pressure higher than the bubble point is applied to the membrane surface, the bubbles present on the membrane surface will be squeezed out of the membrane so that the air-lock phenomenon can be released. Therefore, high permeability can be maintained, and no substantial decrease of the flux permeated through a membrane will occur.

[0012]

Also, in the full-filtration type liquid filtering device connected to a liquid supply tank having a bypass valve connected in the filtering device or in front of the filtering device and having a hydrophilized membrane made of a fluorine type high-molecular-weight polymer installed in a container, the bypass valve is opened intermittently during the pressurized filtration of the liquid to be treated so that the pressure in the container drops significantly. In this method, the operation can be performed under a pressure below the bubble point. The air-lock

phenomenon can be released depending on the significant pressure variation on the upstream side of the membrane surface (liquid supply side). In other words, the bubbles mixed into or generated in the membrane have their volume increased due to the significant pressure drop and are squeezed out through the bypass valve connected into the filtering device or to the front of the filtering device. If the time of the period for opening/closing the bypass valve is too short, a good effect cannot be obtained. Therefore, the time for decreasing the pressure by opening the bypass valve is preferred to be in the range of 10 sec – 1 min. The time of one opening/closing cycle is preferred to be in the range of 3-10 min. However, said time range varies depending on the type of the liquid to be treated, and an appropriate time range can be set easily by those who are familiar with this technology.

[0013]

Application examples

The circulating filtration method for a liquid filtering device disclosed in the present invention will be explained based on figures. Figure 1 shows an example of the device used for implementing the method of the present invention. Figure 2 shows another example. Symbols 1-2 and 4-7 are the same as those shown in Figure 1. In Figure 1, the liquid to be treated in liquid supply tank 1 is pressurized by pump 2 and is supplied to full-filtration type filtering device 4 having a hydrophilized membrane of a fluorine type high-molecular-weight polymer installed in a container. At that time, the filtration pressure is adjusted by using pressure adjusting valve 6 while measuring the pressure with pressure gauge 5. The flux permeated through a membrane is measured by flowmeter 7. As shown in Figure 2, bypass valve 3 is connected to filtering device 4. When bypass valve 3 is opened intermittently to feed back the liquid to be treated to liquid supply tank 1, the pressure in filtering device 4 drops significantly. Said bypass valve 3 can also be connected to the front of the filtering device. In the following, the present invention will be explained in more detail with reference to application examples. The present invention, however, is not limited to these application examples.

[0014]

<u>Application Example 1</u>

A fluorine-type high-molecular-weight polymer membrane (tetrafluoroethylene porous membrane produced by Nitton Denko K.K., product name: Nitrofron NTF1121, average pore size 0.1 μm) was immersed in methanol and water sequentially for 10 min in each liquid, followed by being immersed in 4.1 wt% aqueous boric acid solution for 10 min. The pores were impregnated with the aqueous boric acid solution. After a low-pressure mercury lamp with an output of 50 W was radiated on said membrane for 60 sec, the membrane was washed with pure

water and then dried, obtaining a hydrophilized membrane. The bubble point of the obtained membrane in the aqueous system was 7.2 kg/cm^2. The membrane was used to perform full-filtration type pressurized filtration to a liquid mixture of ammonia:hydrogen peroxide water:pure water = 1:1:5 using the device shown in Figure 1 at liquid temperature of 25°C under an operating pressure of 10 kg/cm^2. If the value calculated by dividing the flux permeated through a membrane by the operating pressure was called the permeation coefficient, the initial permeation coefficient was 7.2 cm^3/cm^2/sec/(kg/cm^2). After 1 h, the permeation coefficient was 7.1 cm^3/cm^2/sec(kg/cm^2), which showed little change.

[0015]

Comparative Example 1

Full-filtration type pressurized filtration was carried out in the same way as described in Application Example 1 except that the operating pressure was changed to 3 kg/cm^2. The initial permeation coefficient was 6.5 cm^3/cm^2/sec(kg/cm^2). After 1 h, the permeation coefficient became 2.1 cm^3/cm^2/sec(kg/cm^2), which decreased significantly due to air lock.

[0016]

Application Example 2

The same hydrophilized membrane and liquid mixture used in Application Example 1 were used. Bypass valve 3 was opened intermittently by using the device shown in Figure 2, and full-filtration type pressurized filtration was performed at a liquid temperature of 25°C and under an operating pressure of 2 kg/cm^2. During the filtration operation, the pressurization filtration was performed for 4 min 50 sec, and the pressure decrease realized by intermittently opening bypass valve 3 lasted 10 sec. The period was 5 min. The initial flux permeated through a membrane was 16 cm^3/cm^2/sec. The flux permeated through a membrane after 1 h was 15.8 m^3[sic]/cm^2/sec, which showed little change.

[0017]

Comparative Example 2

Full-filtration type pressurized filtration was performed in the same way as described in Application Example 2 except that bypass valve 3 was not opened. The initial flux permeated through a membrane was 13 cm^3/cm^2/sec. The flux permeated through a membrane after 1 h was 4.2 cm^3/cm^2/sec, which decreased significantly due to air lock.

[0018]

Effect of the invention

According to the present invention, during circulating filtration performed by a full-filtration type liquid filtering device having a hydrophilized membrane of a fluorine type high-molecular-weight polymer installed in a container, the problem of a decrease in the flux permeated through a membrane caused by air lock due to the bubbles mixed into or generated in the membrane can be solved, and the flux permeated through a membrane can be maintained in the initial state.

[0019]

Brief description of the figures

Figure 1 is a schematic diagram illustrating an example of the device used for implementing the method of the present invention.

Figure 2 is a schematic diagram illustrating an example of another device used for implementing the method of the present invention.

Explanation of symbols

1 Liquid supply tank
2 Pump
3 Bypass valve
4 Full-filtration type filtering device
5 Pressure gauge 5
6 Pressure adjusting valve
7 Flowmeter

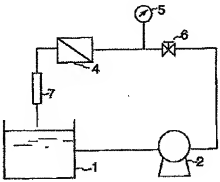


Figure 1

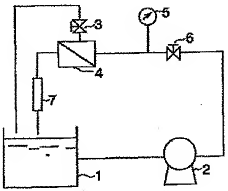


Figure 2